ABSTRACT

Title:

Radiative Lifetime and Quenching Kinetics for the XeF (B 1/2) State, C.H. Fisher and R.E. Center, Mathematical Sciences Northwest, Inc.--A state-selective laser-induced-fluorescence technique has been used to determine the radiative lifetime and quenching kinetics for the XeF (B 1/2) excited state. Fluorine atoms are formed by flash dissociating a mixture of UF_6 and Xe in He. After a suitable delay to allow recombination of Xe and F atoms, ground state XeF molecules are excited to the XeF (B 1/2) state by passing a 3511 Å XeF laser beam through the cell. The fluorescence decay at 3533 Å is monitored perpendicular to the exciting light using a spectrometer-photomultiplier combination. Quenching rate coefficients for the collision partners He, Ne, Xe, F_2, and NF_3 have been determined. Fluorescence emission at 460 nm due to collisional transfer from the XeF (B 1/2) to the XeF (C 1/2) state has also been observed.

*Supported by DARPA Order No. 1806, ONR Contract No. N00014-76-C-1066.

MSNW KINETICS PROGRAM--RARE GAS HALIDES

- BASIC KINETICS MEASUREMENTS IN SUPPORT OF DARPA SCALE-UP PROGRAMS

  - MEASUREMENT OF RADIATIVE LIFETIME AND COLLISIONAL QUENCHING RATE CONSTANTS

  - DATA YIELD SATURATION FLUX NECESSARY FOR SYSTEM DESIGN

- PROGRAM EMPHASIZES XeF KINETICS

  - WAVELENGTH IN NEAR UV (PREFERABLE TO KrF)

  - POSSIBILITY OF DEVELOPING VISIBLE LASER ON C-X TRANSITION

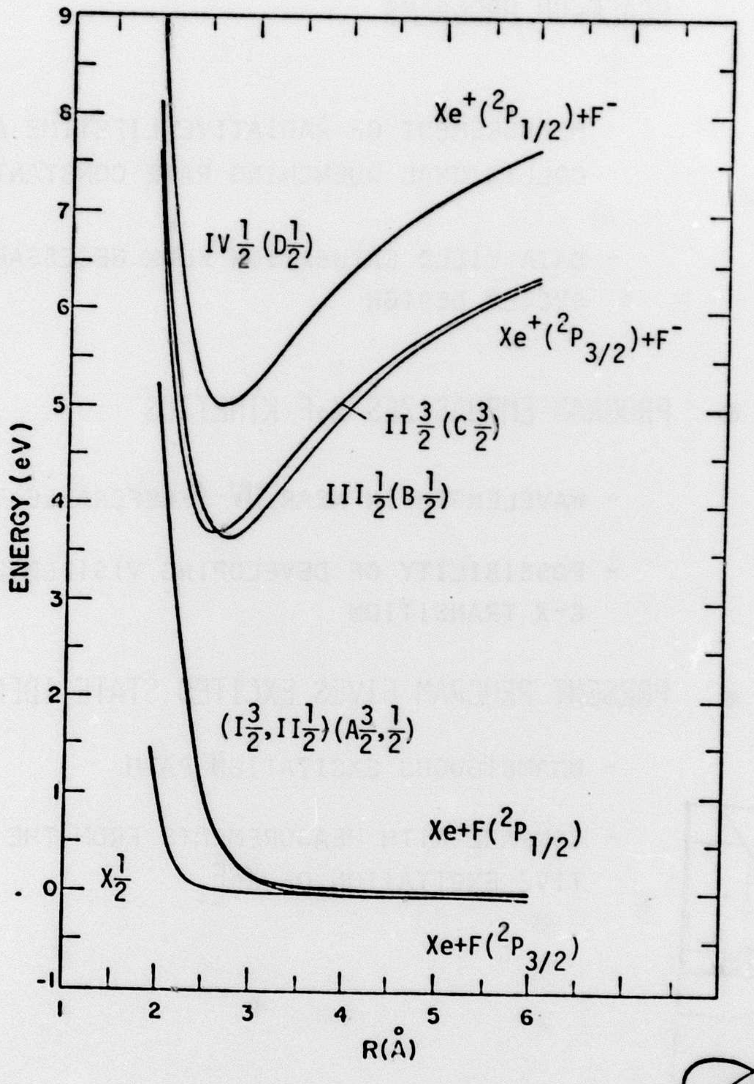
- PRESENT PROGRAM GIVES EXCITED STATE IDENTIFICATION

  - UNAMBIGUOUS EXCITATION PATH

  - COMPARE WITH MEASUREMENTS FROM THE DISSOCIATIVE EXCITATION OF XeF_2

XeF POTENTIAL ENERGY CURVES

T. H. Dunning and P. J. Hay, to be published



EXPERIMENTAL CONCEPT

- PRODUCE F ATOMS BY FLASH PHOTOLYSIS IN PRESENCE OF Xe

  e.g. $F_2 + h\nu \rightarrow 2F$

- WAIT FOR RECOMBINATION INTO GROUND ELECTRONIC STATE

  $Xe + F + (M) \rightleftarrows X\ F(B\tfrac{1}{2}) + (M)$

  (DELAY TIME MUST BE LESS THAN TIME FOR F-ATOM RECOMBINATION OR LOSS BY DIFFUSION)

- EXCITE $XeF(X\tfrac{1}{2})$ BY XeF LASER ON B-X TRANSITION

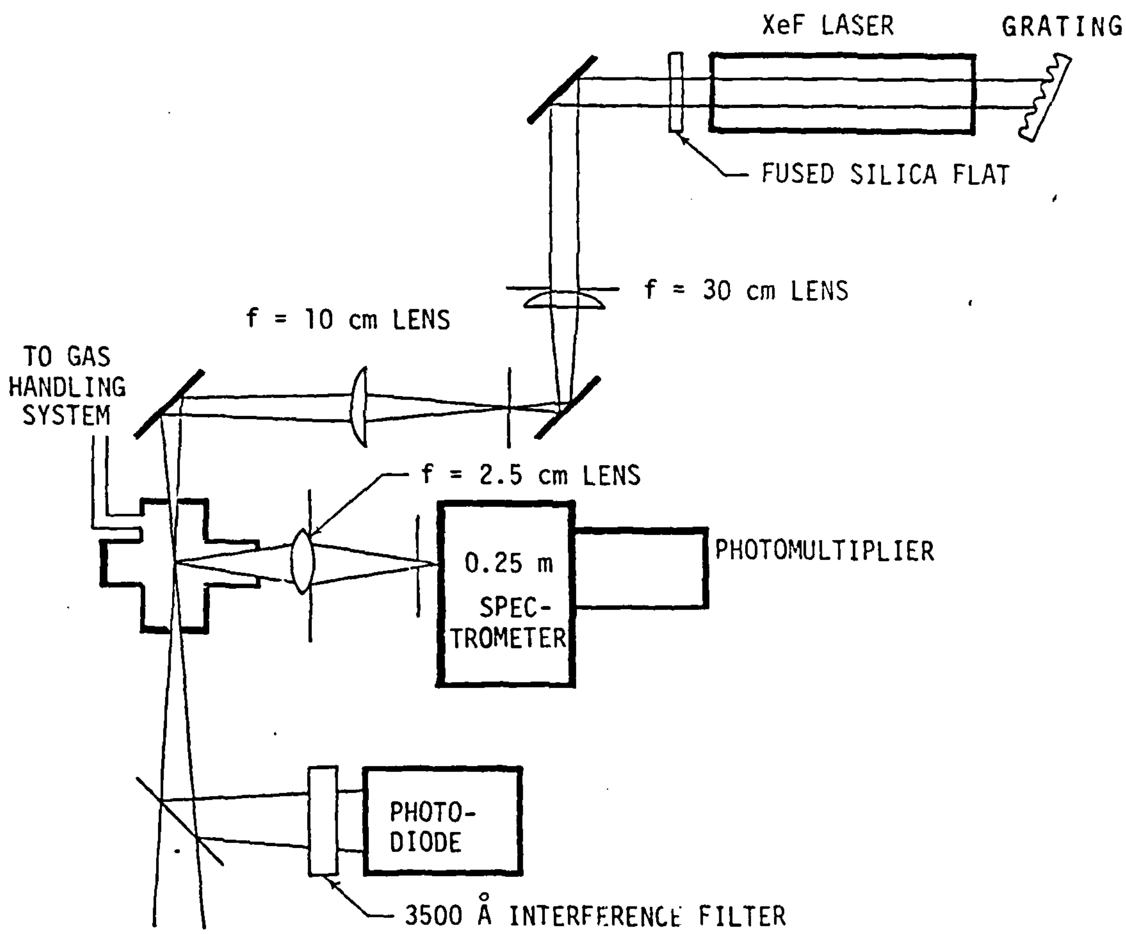
  $XeF_{v''}(X\tfrac{1}{2}) + h\nu \rightarrow XeF(B\tfrac{1}{2})$

- MONITOR FLUORESCENCE DECAY--COMPETITION OF RADIATIVE DECAY AND COLLISIONAL QUENCHING

  $XeF\ (B\tfrac{1}{2}) \rightarrow XeF(X\tfrac{1}{2}) + h\nu$

  $XeF\ (B\tfrac{1}{2}) + M \rightarrow XeF(X\tfrac{1}{2}) + M$

SCHEMATIC DIAGRAM FOR THE OPTICAL SETUP FOR THE LASER INDUCED FLUORESCENCE EXPERIMENT



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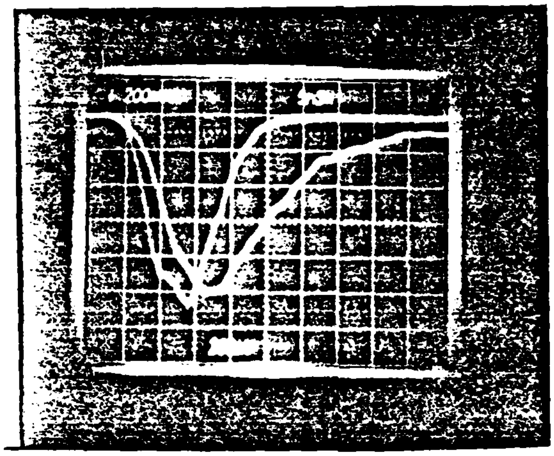
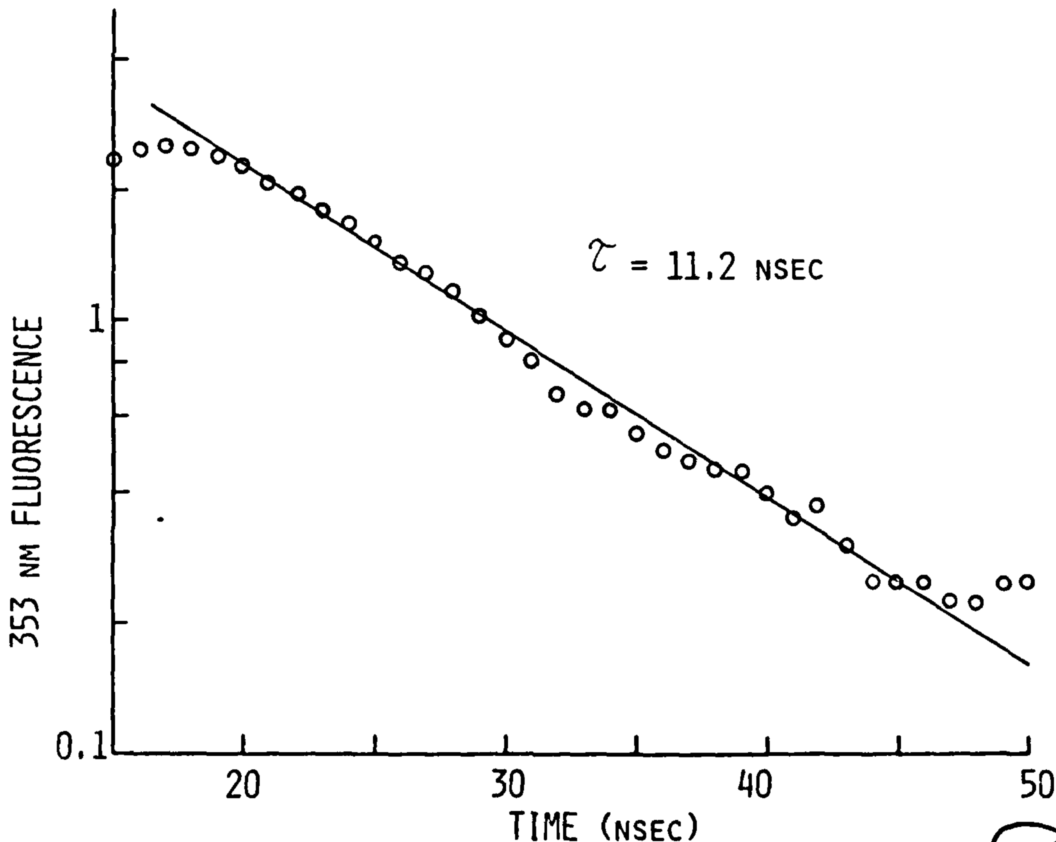
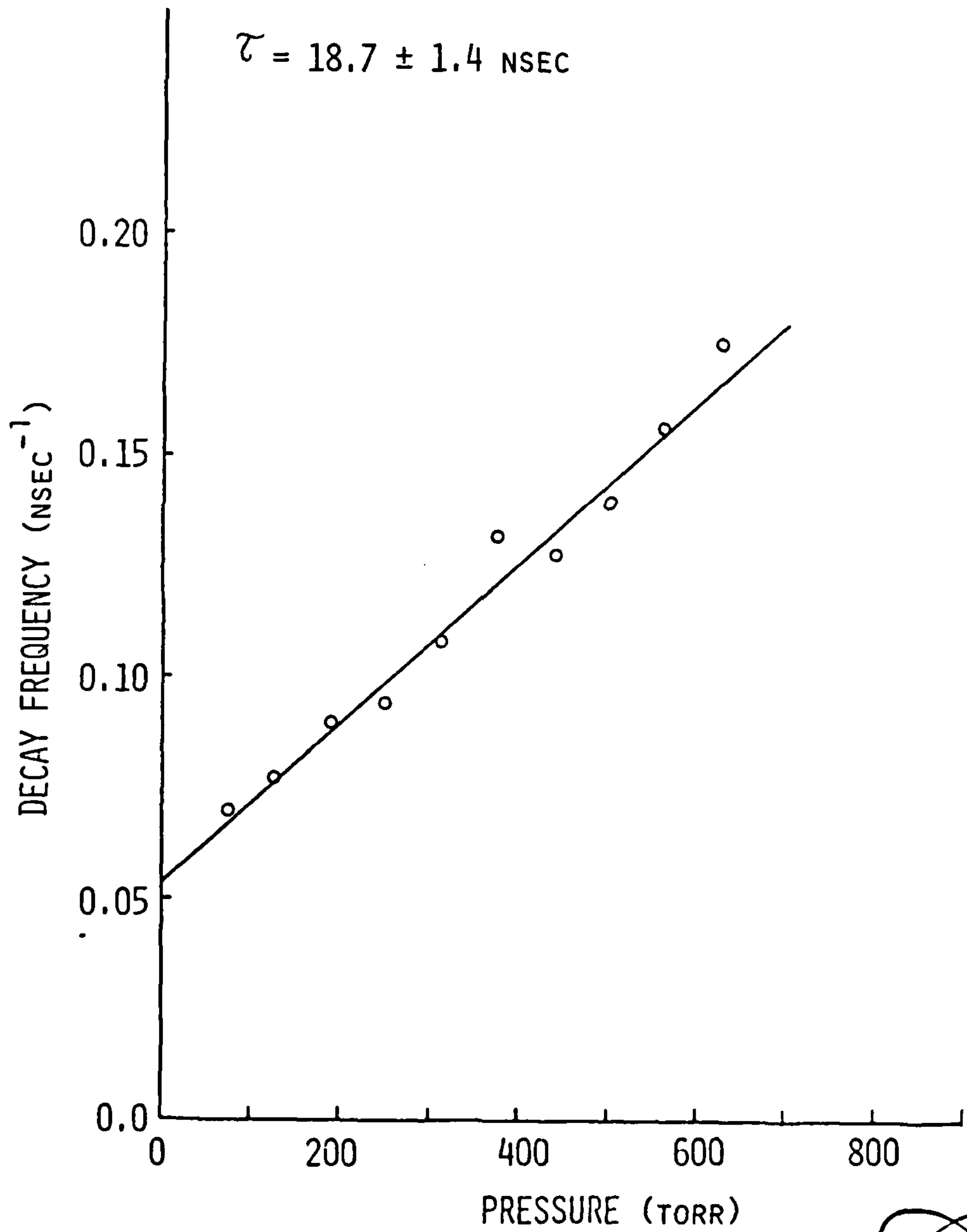
353 NM FLUORESCENCE FROM

125 TORR He + 10 TORR Xe + 0.7 TORR UF_6



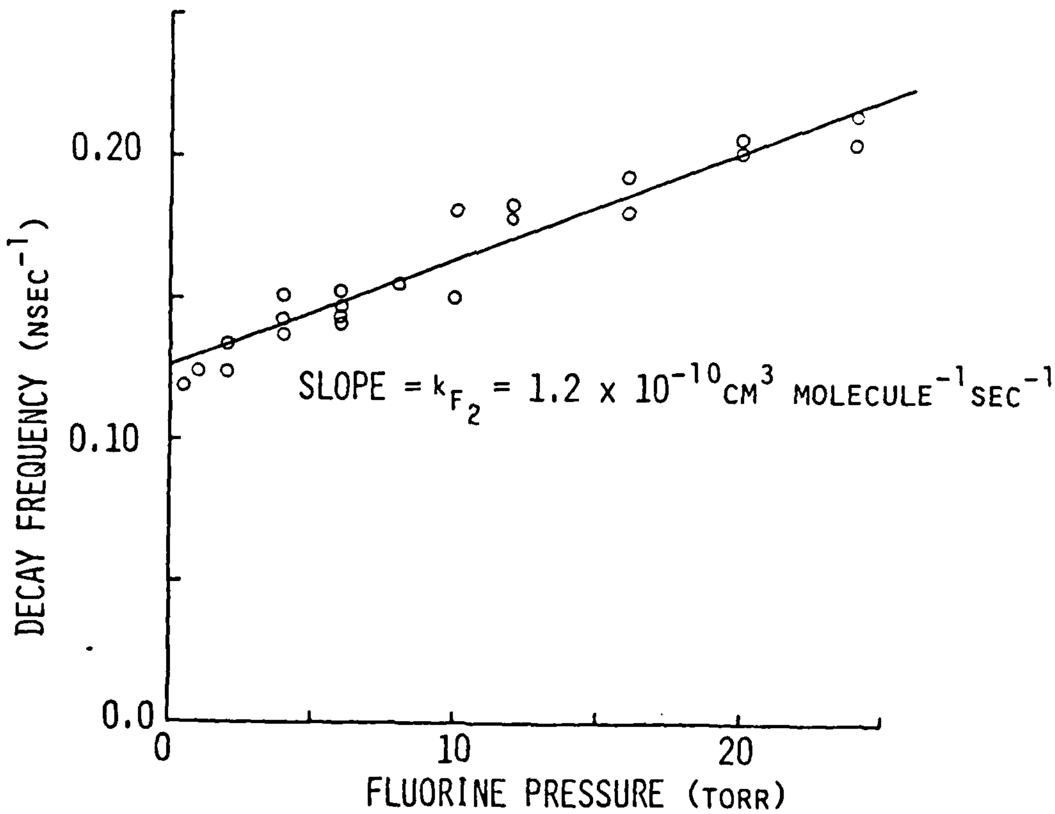


$XeF(B\frac{1}{2})$ FLUORESCENT LIFETIME MEASUREMENTS



$XeF(B\frac{1}{2})$ QUENCHING BY F_2

250 TORR He + 10 TORR Xe + 0.3 TORR UF_6



SUMMARY OF XeF($B\frac{1}{2}$) RADIATIVE LIFETIME AND QUENCHING DATA

- XeF($B\frac{1}{2}$) $\tau_r = 18.7 \pm 1.4$ NSEC

- XeF($B\frac{1}{2}$) TWO BODY QUENCHING RATE CONSTANTS

MOLECULE	k_q(CM^3 MOLECULE^{-1} SEC^{-1})	PRESSURE RANGE (TORR)
He	2×10^{-12}	75 - 750
Ne	$\lesssim 1.4 \times 10^{-13}$	75 - 750
Xe	6×10^{-11}	5 - 80
F_2	1.2×10^{-10}	0.5 - 24
NF_3	3×10^{-12}	15 - 500
~~UF_6*~~	~~$< 1 \times 10^{-11}$~~	~~0.3 - 2~~

~~* PRELIMINARY UPPER BOUND ESTIMATES~~

XeF POTENTIAL ENERGY CURVES

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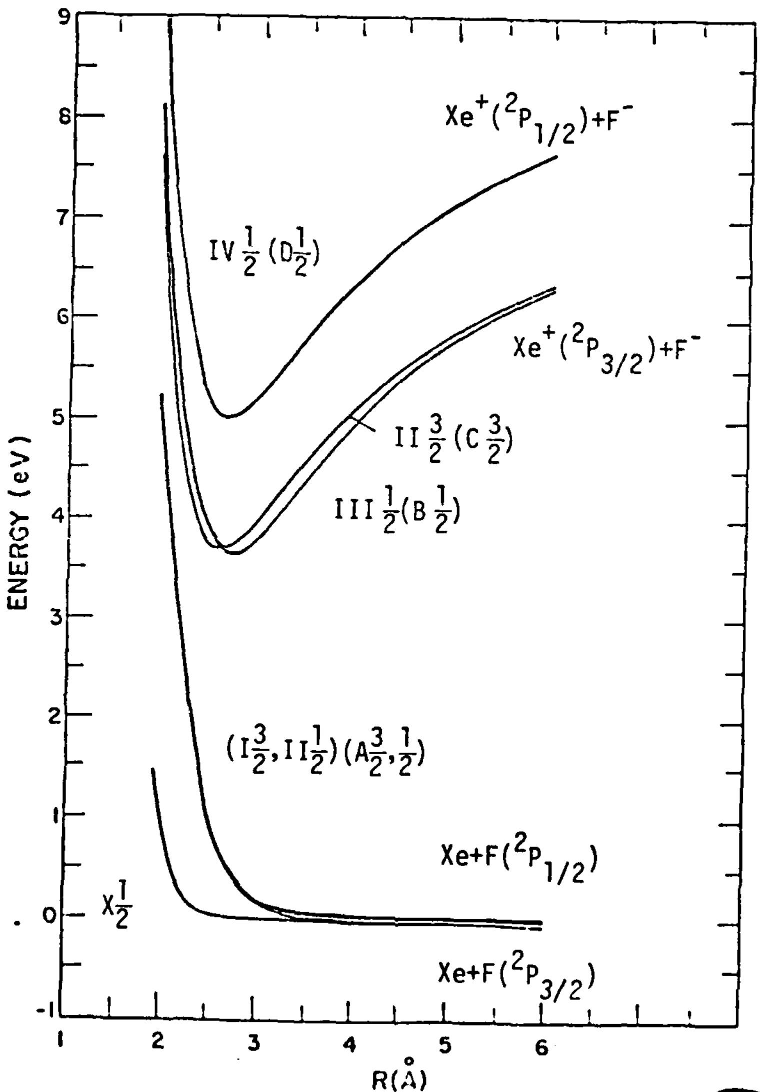
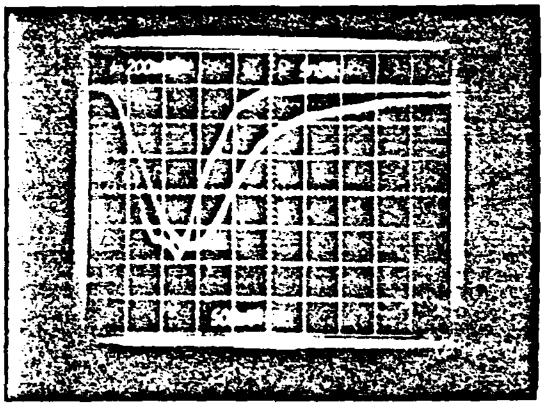
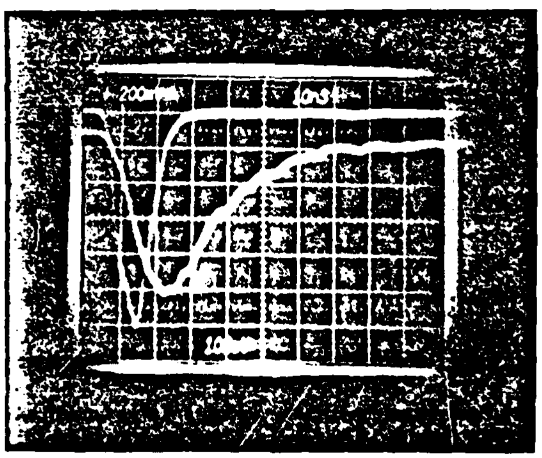


COMPARISON OF XeF FLUORESCENCE AT 460 AND 353 NM



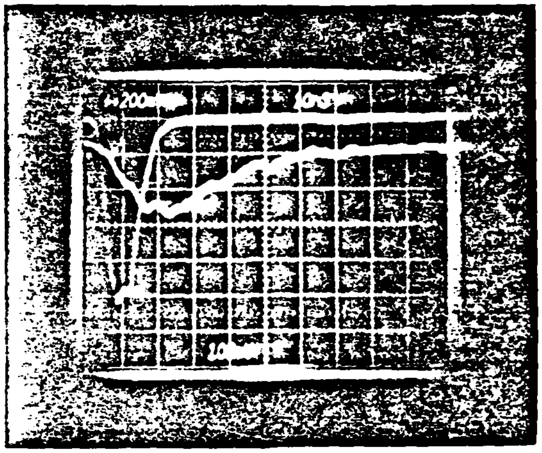
(A) 353 nm



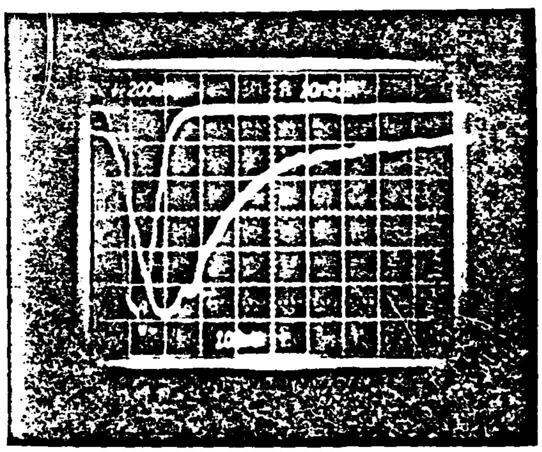
(B) 460 nm

1.5 atm He + 10 TORR Xe + 0.7 TORR UF_6

EFFECT OF Ar CONCENTRATION ON 460 nm FLUORESCENCE



(A) 250 TORR Ar + 10 TORR Xe + 0.7 TORR UF_6



(B) 625 TORR Ar + 10 TORR Xe + 0.7 TORR UF_6

DATA INTERPRETATION

$$XeF(B\tfrac{1}{2}) + M \rightarrow XeF(X\tfrac{1}{2}) + M \qquad (1)$$

$$XeF(B\tfrac{1}{2}) \xrightarrow{\tau_B} XeF(X\tfrac{1}{2}) + h\nu \text{ (353 NM)} \qquad (2)$$

$$XeF(C\tfrac{1}{2}) + M \rightarrow XeF(A\tfrac{3}{2},\tfrac{1}{2}) + M \qquad (3)$$

$$XeF(C\tfrac{1}{2}) \xrightarrow{\tau_C} XeF(A\tfrac{3}{2},\tfrac{1}{2}) + h\nu \text{ (460 NM)} \qquad (4)$$

$$XeF(B\tfrac{1}{2}) + M \underset{k_e'}{\overset{k_e}{\rightleftharpoons}} XeF(C\tfrac{1}{2}) + M \qquad (5)$$

PROCESSES (1 - 5) $\longrightarrow$ DOUBLE EXPONENTIAL DECAY WITH TIME CONSTANTS

$\lambda_1, \lambda_2(k_1, k_3, \tau_B, \tau_C, k_e, k_e')$

IN LIMIT $k_e \longrightarrow 0$

(1,2) $\longrightarrow$ SIMPLE EXPONENTIAL DECAY FOR 353 NM

WITH $\lambda_1 = \frac{1}{\tau_B} + k_1 M$

(3,4) $\longrightarrow$ SIMPLE EXPONENTIAL DECAY FOR 460 NM

WITH $\lambda_2 = \frac{1}{\tau_C} + k_3 M$

IN LIMIT $k_e \longrightarrow \infty$

BOTH STATES DECAY WITH SAME TIME CONSTANT

$\lambda_2(\tau_B, \tau_C, k_e, k_i)$

LASER IMPLICATIONS

- SATURATION FLUX $\Phi_S = \frac{h\nu}{\sigma_{s.e.}} \left(\frac{1}{\tau_B} + \sum_i kq_i \; Q_i \right)$

  FOR Ar + 1% Xe + 0.3% F_2 MIXTURES

  $$\Phi_S = 150 \text{ kW/cm}^2 \text{ AT 1 ATM}$$

  $$\Phi_S = 230 \text{ kW/cm}^2 \text{ AT 2 ATM}$$

- COMPARISION OF OPTICAL EMISSION PROPERTIES AT 351 NM AND 460 NM

WAVELENGTH (NM)	351	460
LIFETIME (NSEC)	18.7	113*
BANDWIDTH (NM)	2	47*
CROSS SECTION(CM^2)	$\overset{5}{4}\times10^{-16}$	$\cancel{\sim 7\times10^{-18}}$ $\sim 1\times10^{-17}$

*FROM THEORETICAL CALCULATIONS BY T.H. DUNNING, JR. AND P.J. HAY.

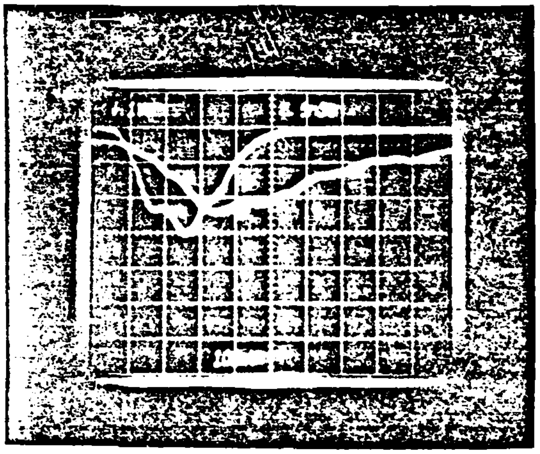
- FOR EFFICIENT 460 NM LASER, MUST FIND MOLECULE M SUCH THAT

  $$XeF(B\tfrac{1}{2}) + M \overset{k_e}{\rightleftharpoons} XeF(C\tfrac{3}{2}) + M$$

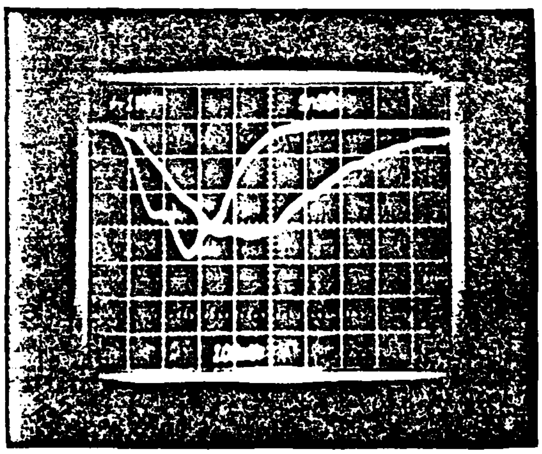
  WITH $k_e[M] \cdot\cdot \frac{1}{\tau_B} + k_q^B \, Q$

EFFECT OF XENON CONCENTRATION ON

460 nm FLUORESCENCE



(A) 250 TORR He + 20 TORR Xe + 0.7 TORR UF_6



(B) 250 TORR He + 30 TORR Xe + 0.7 TORR UF_6

CONCLUSIONS

(1) Ne IS PREFERABLE TO Ar AS DILUENT

- SMALLER QUENCHING CROSS SECTION
- NO INTRINSIC ABSORPTION (NRL DATA)

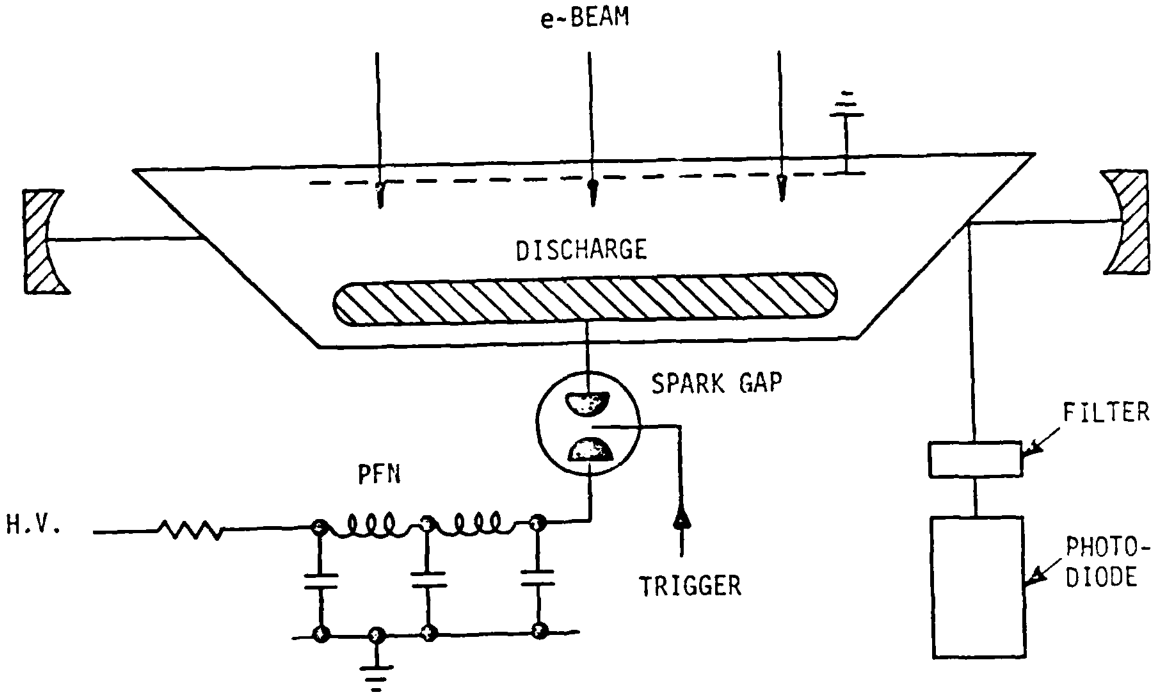
(2) STATE IDENTIFIED LIFETIME MEASUREMENT

$\tau \simeq 18$ nsec FOR B STATE

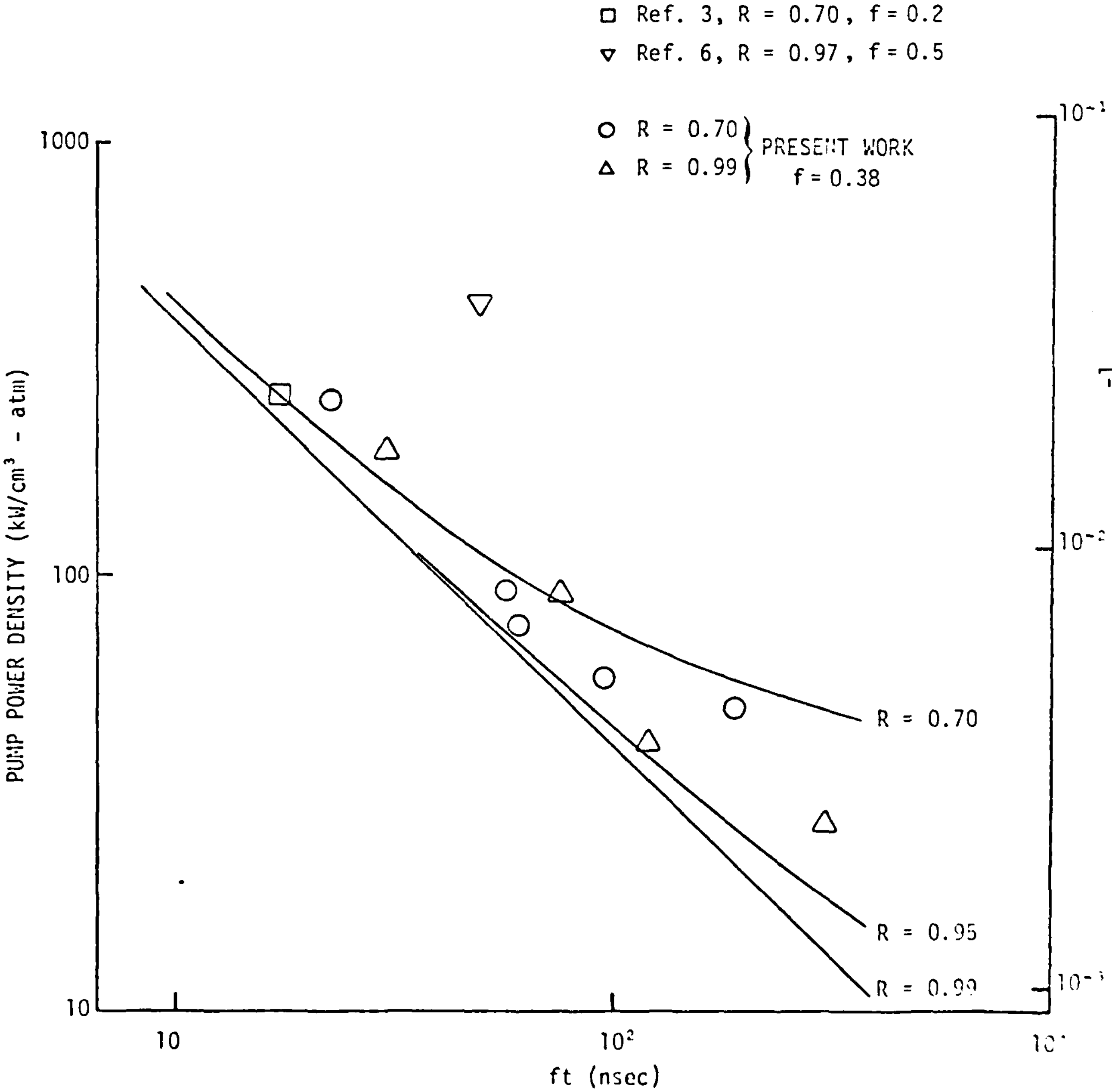
(3) REQUIREMENTS FOR POTENTIAL VISIBLE XeF LASER AT 460 nm

- RADIATIVE LIFETIME MEASUREMENT
- IDENTIFICATION OF EFFECTIVE COLLISION PARTNER TO POPULATE C STATE

EXPERIMENTAL LAYOUT FOR KrF AND XeF THRESHOLD PUMPING MEASUREMENTS



THRESHOLD POWER DENSITY MEASUREMENTS IN
ε-BEAM SUSTAINED DISCHARGES



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30 August 1977

Check with → Behringer
If OK prepare approval

Mr. R. H. Register
Contracting Officer
Office of Naval Research
Department of the Navy
800 North Quincy Street
Arlington, VA 22217

Dear Mr. Register:

N00014-76-C-1066 NR 395-568
MSNW Project 1062

Enclosed for your review are 5 copies of an abstract and viewgraphs entitled, "Radiative Lifetime and Quenching Kinetics for the XeF (B 1/2) State," by C. H. Fisher and R. E. Center. We request permission to submit this abstract and viewgraphs for presentation at the Thirtieth Annual Gaseous Electronics Conference, 18-21 October 1977. A paper would not be written for this presentation.

We would appreciate receiving your approval as soon as possible. Thank you for your assistance.

Sincerely yours,

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Sally Ann Mowrey

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